

FIG. 1. Reaction cross section (σ^R) as a function of the total energy E for different vibrational states of H_2^+ . The inset shows the corresponding experimental results reproduced from Ref. 15. Note that while the inset has the same scale as the main figure along the ordinate, the scales are different along the abscissa.

dependence of the cross section for the collision-induced dissociation process



Details of the analytic fit, the QCT calculation, and the results, along with results of a QM investigation of reactive resonances in collinear $\text{He}-\text{H}_2^+$ collisions will be published subsequently.

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¹(a) B. Liu, *J. Chem. Phys.* **58**, 1925 (1973); (b) P. Siegbahn and B. Liu, *ibid.* **68**, 2457 (1978); (c) D. G. Truhlar and C. J. Horowitz, *ibid.* **68**, 2466 (1978); **71**, 1514(E) 1979.

²B. C. Garrett and D. G. Truhlar, *Proc. Natl. Acad. Sci. U.S.A.* **76**, 4755 (1979); *J. Chem. Phys.* **72**, 3460 (1980).

³(a) H. R. Mayne and J. P. Toennies, *J. Chem. Phys.* **75**, 1794 (1981); (b) N. C. Blais and D. G. Truhlar in *Potential Energy Surfaces and Dynamics Calculations*, edited by D. G. Truhlar (Plenum, New York, 1981).

⁴R. B. Walker, E. B. Stechel, and J. C. Light, *J. Chem. Phys.* **69**, 2922 (1978).

⁵(a) M. Kneba, V. Wellhausen, and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.* **83**, 940 (1979); (b) G. P. Glass and B. K. Chaturvedi, *J. Chem. Phys.* **77**, 3478 (1982).

⁶(a) C. T. Rettner, E. E. Marinero, and R. N. Zare, in *Physics of Electronic and Atomic Collisions: Invited papers from the XIII ICPEAC, Berlin, July 27–August 2, 1983*, edited by J. Eichler, I. V. Hertel, and N. Stollerfoht (North-Holland, Amsterdam, 1984); (b) D. P. Gerrity and J. J. Valentini, *J. Chem. Phys.* **79**, 5202 (1983).

⁷N. C. Blais and D. G. Truhlar, *Chem. Phys. Lett.* **102**, 120 (1983).

⁸W. A. Chupka and M. E. Russell, *J. Chem. Phys.* **49**, 5426 (1968); (b) W. A. Chupka, J. Berkowitz, and R. E. Russell, *Sixth International Conference on the Physics of Electronic and Atomic Collisions* (M.I.T., Cambridge, MA, 1969), p. 71.

⁹H. A. Schuessler, Jr. (private communication).

¹⁰W. N. Whitton and P. J. Kuntz, *J. Chem. Phys.* **64**, 3624 (1976).

¹¹P. J. Brown and E. F. Hayes, *J. Chem. Phys.* **55**, 922 (1971).

¹²D. R. McLaughlin and D. L. Thompson, *J. Chem. Phys.* **70**, 2748 (1979).

¹³Tomi Joseph, Ph.D. thesis, Indian Institute of Technology, Kanpur 208016, India, 1983.

¹⁴K. S. Sorbie and J. N. Murrell, *Mol. Phys.* **29**, 1387 (1975).

¹⁵R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics* (Oxford University, New York, 1974).

¹⁶V. Paček, U. Havemann, Z. Herman, F. Schneider, and L. Züllicke, *Chem. Phys. Lett.* **49**, 273 (1977).

High energy CH-overtone spectra of benzene at 1.8 K

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It is now well established that the transition energies of CH-stretching overtones in large molecules can be fit to the Birge-Sponer relationship.¹ The description of the bandwidths of these transitions, however, has not been as clearly ascertained. Previous experimental work has determined the

homogeneous broadening (from Lorentzian line shape fits) of the CH-stretch overtones of benzene² and naphthalene³ in the gas phase and low-temperature (2 °K) crystals, respectively. In a subsequent study⁴ of durene (tetramethylbenzene) at low temperature (~2 K), a rather large difference in

the bandwidths of methyl bands (25 cm^{-1}) compared to the aromatic band ($\sim 100\text{ cm}^{-1}$) at $\Delta\nu = 5$ was found. The contributions of energy and phase relaxation to the homogeneous broadening have been discussed recently.⁴ At room temperature, both types of bands are rather broad ($\sim 200\text{ cm}^{-1}$) and approach the linewidth usually observed for liquids which have a significant congestion due to, e.g., librational sequence progressions.⁵

Benzene overtone spectroscopy has been the subject of many theoretical and experimental studies of the gas and liquid phases. However, due to some experimental difficulties the overtone spectra of benzene at very low temperatures have not previously been reported. In this Communication we report on such a measurement for $\Delta\nu = 5$ at 1.8 K. We resolve the observed spectrum into three bands and obtain the individual local mode linewidths. The widths ($\sim 70\text{--}130\text{ cm}^{-1}$) are comparable to the widths of gas-phase benzene reported by Bray and Berry, and compares well with the width of other aromatic CH-transition studies by us at low temperature. Thus low-temperature measurement on benzene shows the intrinsic nature of the width of the CH overtones and the absence of thermal congestion contribution, a point which has been of some concern recently.⁶ Finally, we provide results on related molecules at low temperature for comparison.

The spectroscopic methods have been described previously.^{3,4} The benzene crystals were grown by very slowly lowering the sample into a Dewar with a decreasing temperature gradient achieved with solid CO_2 at bottom. The single crystals, which showed good optical quality, were cut in a cold glove bag and transferred to an optical Dewar pre-cooled to $\sim 100\text{ K}$. The Dewar was evacuated to a lower pressure to allow slower cooling. The crystals were then immersed in liquid He which was cooled to below the λ transition by pumping.

The sensitivity of the direct-absorption double-beam spectrometer, which used phase sensitive detection, allowed an optical density of ~ 0.003 to be recorded at 1:1 signal to noise with a resolution of 0.3 cm^{-1} . Finally, the line shapes were analyzed using a nonlinear least-squares fitting routine.

Figure 1 shows the $\Delta\nu_{\text{CH}} = 5$ overtone spectrum at 1.8 K along with the fitted sum of Lorentzians and components. The benzene linewidths are presented in Table I along with results for the other molecules studied.

Several important conclusions can be drawn from these results. The benzene spectrum displays an overall width of $225 \pm 10\text{ cm}^{-1}$ at $\sim 100\text{ K}$ which resolves into three bands at 1.8 K. The benzene crystal is known to have a site symmetry of C_i ⁷ and inhomogeneous broadening of less than a few cm^{-1} .⁸ In the rigorous site symmetry the six CH local modes of benzene split into three pairs. It is therefore expected that three bands would be observed as is actually found experimentally.

The linewidths of the low-temperature benzene bands are quite similar to the gas phase linewidths ($\sim 100\text{ cm}^{-1}$). We conclude from this result that the aromatic CH stretch ($\Delta\nu = 5$) overtones have an intrinsic width of a minimum of 70 cm^{-1} . Furthermore, in contrast to the durene methyl overtones with a width as low as 25 cm^{-1} , the aromatic CH

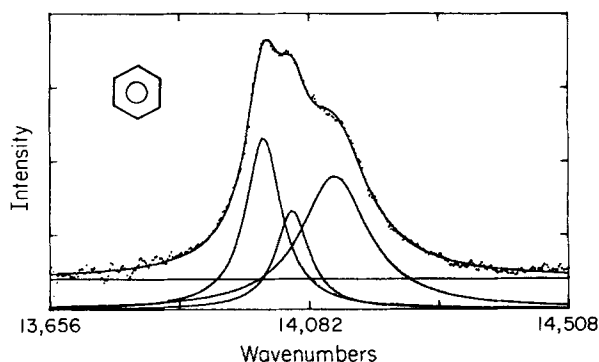


FIG. 1. Direct CH-stretching overtone absorption spectrum ($\Delta\nu = 5$) of benzene at 1.8 K. The crystal path length was about 4 cm. The points are the experimental data and the solid lines are the best fit sum of Lorentzians and the components. The spectral resolution for this scan was $\sim 5\text{ cm}^{-1}$. The intensity, which gives the relative absorbance, is in arbitrary units.

width of benzene is much broader and compares with that of the durene aromatic CH. Tetrachlorobenzene has only two CH's related by the inversion symmetry and since the site symmetry is again C_i only one band is predicted. For $\Delta\nu = 5$ we observe one main band and a smaller one ($A_{\text{rel}} \sim 0.2$) with widths of ~ 80 and 45 cm^{-1} , respectively, which are in Fermi resonance.

With this analysis in mind we examined the results of the naphthalene $\Delta\nu_{\text{CH}} = 5$ spectra. In our previous work we fit the naphthalene- h_8 spectrum with two Lorentzians and the partially deuterated naphthalene- $\alpha-d_4$ again showed two Lorentzians with the higher energy band substantially reduced in intensity. The higher energy N- $\alpha-d_4$ band was taken to be due to residual α -hydrogens. However, recent quantitative NMR analysis shows the residual α -H content of the N- $\alpha-d_4$ to be $< 5\%$ so that it could not be the source of the observed higher energy. Considering the rigorous site symmetry of naphthalene (C_i) we expect further splitting of the β -CH's just as discussed for benzene.⁹ Analysis of the N- h_8 spectrum using three Lorentzians was performed and the fit

TABLE I. Low-temperature ($\leq 2\text{ K}$) bandwidth and position of CH overtones ($\Delta\nu = 5$) of large aromatic molecules.

Molecule	Band	$\bar{\nu}(\text{cm}^{-1})$	FWHM (cm^{-1})	A_{rel}
Benzene	α	14123 (4)	133 (10)	0.7
	β	14053 (5)	65 (10)	0.3
	γ	14007 (4)	70 (06)	1.0
1,2,4,5-tetra chlorobenzene ^a	α	14226 (4)	77 (08)	1.0
	α^b	14289 (4)	45 (05)	0.2
naphthalene- H_8 ^a	α	14055 (2)	133 (10)	3.0
	β	13952 (4)	90 (10)	1.0
- 1,4,5,8- d_4 ^a	β'	14036 (8)	113 (10)	1.0
	β	13952 (3)	66 (07)	0.9
durene aromatic methyl ^c	α	13872 (4)	103 (06)	...
	a	13620 (4)	43 (05)	~ 1
	b	13532 (4)	25 (04)	~ 1
	c	13344 (4)	50 (05)	~ 2

^a Parameters given for two peak fit to spectrum.

^b Combination band in Fermi resonance.

^c Assignments have been presented in Ref. 4. Note the difference in bandwidth between aromatic band (α) and methyl bands (a, b, c).

was quite good.¹⁰ The width parameters of the higher and lower energy bands did not change appreciably from those reported previously. The primary change was the relative intensity which is now consistent with the isotopic composition. Finally, it is interesting to note the narrowing of the benzene CH overtone in going from the liquid phase to the vapor or low temperature solid. In the former phase the width is 223 cm^{-1} ,¹¹ while in the latter two it is $\sim 100^2$, 70 – 130 cm^{-1} , respectively.

The important question is what causes the intrinsic broadening of the gas and cold molecules? Armed with the durene data we have attributed the broadening to population relaxation. We showed previously⁴ that the ratio of methyl to aromatic linewidths did not quantitatively scale with an estimate of the local-bath total density of states. However, qualitatively, the total density of states for the aromatic ring was much higher than for the methyl group so it is reasonable that the aromatic CH's relax faster to the bath.¹² We expect the effective coupling of aromatic CH overtone to the bath to be greater than for the methyl CH's. This idea seems to be borne out by recent quantitative theoretical calculations¹³ where the coupling of the CH stretch to bending modes is modeled via the *G*-matrix coupling. The coupling in this model is due to the stretch coordinate dependence of the effective mass for bending motions (or possibly other modes) involving significant displacements of the CH bond.

In conclusion, we have obtained the very low temperature (1.8 K) overtone spectra of the prototypical aromatic molecule, benzene, the only molecule for which the overtones have now been studied in all phases. The aromatic CH bands remain relatively broad ($\sim 100\text{ cm}^{-1}$) even at 1.8 K in contrast to aliphatic methyl bands (of durene) which become narrower by up to a factor of 4. The fact that both gas phase

and low-temperature bandwidths of aromatic CH's are similar indicates that the thermal congestion is not the origin of benzene widths and that it is certainly possible to obtain information on the dynamics of CH overtones in benzene (or comparable molecules) from the spectra. A full account of this work will be published later.

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¹H. L. Fang and R. L. Swofford, in *Advances in Laser Spectroscopy*, edited by B. Garetz and J. Lombardi (Heyden, Philadelphia, 1982), Vol. 1.

²R. Bray and M. J. Berry, *J. Chem. Phys.* **71**, 4909 (1979); K. V. Reddy, D. F. Heller, and M. J. Berry, *ibid.* **76**, 2814 (1982).

³J. W. Perry and A. H. Zewail, *J. Chem. Phys.* **70**, 582 (1979).

⁴J. W. Perry and A. H. Zewail, *J. Phys. Chem.* **86**, 5197 (1982).

⁵G. M. Korenowski and A. C. Albrecht, *Chem. Phys.* **38**, 239 (1979).

⁶G. J. Scherer, K. K. Lehmann, and W. Klemperer, *J. Chem. Phys.* **78**, 2817 (1983).

⁷E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith. *Proc. R. Soc. London, Ser. A* **247**, 1 (1958).

⁸G. C. Nieman and D. S. Tinti, *J. Chem. Phys.* **46**, 1432 (1967).

⁹A higher effective site symmetry along with a Fermi resonance could also give rise to three bands.

¹⁰Unlike benzene spectra, there was no structure on the naphthalene-*h_g* spectrum to define a third band. We fixed the band position, the width and the relative intensity of the center band to the lower energy band according to the values of the *N- α -d₄* spectrum.

¹¹C. K. N. Patel, A. C. Tam, and R. J. Kerl, *J. Chem. Phys.* **71**, 1470 (1979).

¹²D. F. Heller and S. Mukamel, *J. Chem. Phys.* **70**, 463 (1979).

¹³E. L. Sibert III, W. P. Reinhardt, and J. T. Hynes, *Chem. Phys. Lett.* **92**, 455 (1982).

Chemiluminescence produced in the reaction between N (²D, ²P) atoms and HI and HBr, in crossed molecular beam

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Most N atom reactions have been studied extensively in flowing afterglow, flame, and gas discharge experiments¹; also there are a few reports on neutral N atom reactions under single-collision conditions. Love *et al.*² generated N(⁴S, ²D, and ²P) atomic beam by arc heating and crossed it with a beam of halogen molecules ($\text{N} + \text{X}_2 \rightarrow \text{NX} + \text{X}$); Porter *et al.*³ recorded the angular distribution of scattered reaction products from $\text{N} + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$. Here we present the first observation of emission from nascent NH(A ³II),

produced in the reaction of N (²D and ²P) with HI and HBr. An arc heater was used for the production of the metastable N atom beam.

Detail of our apparatus will be described in a forthcoming paper.⁴ Briefly, the system consists of an arc-heated beam source,⁴ constructed following the design of Young *et al.*,⁵ a thermal HX nozzle beam source, and a reaction chamber pumped by a 1200 l/s diffusion pump. A 10% N₂/Ar mixture is admitted into the arc source, heated to (6 500–